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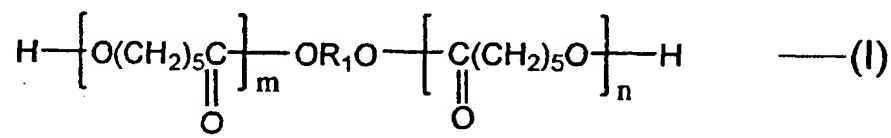
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(54) Method for producing millable polyurethanes and polyurethane elastomers

(57) A method for producing a millable polyurethane, comprises the steps of: producing a poly-ε-caprolactone based diol represented by formula (I)



wherein \square is a caprolactone unit; m and n are numbers of caprolactone units; and R₁ is a divalent group derived from a polymerization initiator of formula R₁(OH)₂, the poly-ε-caprolactone based diol containing a controlled average number of caprolactone units and having a molecular weight distribution Mw/Mn of 1.0 to 1.5; and reacting the poly-ε-caprolactone based diol with a diisocyanate to produce a polyurethane with a restricted crystallizability having a rubber elasticity.

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Description

BACKGROUND OF THE INVENTION

5 FIELD OF THE INVENTION

The present invention relates to a method for producing a millable, polyester polyurethane having an increased resistance to hydrolysis while maintaining strength inherent to polyurethanes.

10 DESCRIPTION OF PRIOR ART

Polyurethane elastomers are classified into castable polyurethanes, millable polyurethanes, thermoplastic polyurethanes. Among them, the castable ones are generally used because they are excellent in various properties. On the other hand, the millable polyurethanes are advantageous in that they can be processed using rolls, presses and the like devices generally employed for processing rubbers.

The castable and thermoplastic polyurethanes are known to be representative examples of segmented elastomers such as thermoplastic elastomers and have both rubber elasticity and wear resistance and strength. When importance is laid on, among others, the strength, wear resistance and the like properties of such polyurethanes, there have been used polyurethanes which comprise soft segments comprising a crystallizable long polyol chain such as polyethylene glycol adipate, polybutylene glycol adipate, polyhexanediol adipate, poly- ϵ -caprolactone and hard segments comprising a polyisocyanate and a short chain polyol and polyamine, with the hard segments preventing the crystallization of the soft segments. More specifically, under usual conditions, the ends of the soft segments are fixed randomly by the hard segments so that the crystallization of the soft segments is prevented to form amorphous polymer chains. As a result, the polymer as a whole exhibits rubber elasticity and when the polymer is deformed excessively, the soft segments, fixed randomly, exhibit orientation crystallizability. Accordingly, polyurethanes vary in the crystal conditions of the soft segments when they are under usual conditions or when they are under excessive deformation. This is why polyurethanes are excellent in wear resistance and strength. Thus, polyurethanes of the castable and thermoplastic types can contain high crystallizability polyols.

On the other hand, in the case of the millable polyurethanes, which do not have those hard segments that are present in the castable or thermoplastic type polyurethanes, use of high crystallizability polyols causes crystallization at low temperatures or at normal temperatures, thus failing to show rubber elasticity. As described above, in designing of the millable polyurethanes, it is impossible to use those polyols that show high crystallizability at ordinary conditions and, hence, various efforts have been made to design polyols so that they have a decreased crystallizability, such as introduction of side chains, random copolymerization, and the like. Under the circumstances, the polyols put in practice include polyester-based ones such as polyethylene propylene adipate and polyethylene butylene adipate, polyether-based ones such as tetrahydrofuran (THF)-alkyl glycidyl ether copolymers, and the like, which are polyols prepared by random polymerization so that structural regularity of the polymer is disturbed to decrease its crystallizability.

Further, the millable polyurethanes are classified into polyester polyurethanes and polyether polyurethanes. Generally, the polyester polyurethanes have low resistance to hydrolysis while the polyether polyurethanes are poor in resistance to thermal aging. The poor resistance to thermal aging of the polyether polyurethanes is an essential problem while the low resistance to hydrolysis of the polyester polyurethanes is not so serious since the resistance to hydrolysis can be improved relatively readily by decreasing the concentration of the ester groups. However, in the case of polyester polyurethanes, use of long straight chain diol adipates such as 1,4-butylene adipate and 1,6-hexylene adipate in order to decrease the concentration of the ester groups results in higher crystallizability so that the resulting polyurethanes cannot be used as millable polyurethanes, particularly at low temperatures, thus failing to give a practically useful polyurethane having a wide range of feasibility. Although poly- ϵ -caprolactone is generally used in castable or thermoplastic type polyurethanes as a raw material for producing hydrolysis resistant polyurethanes, it cannot be used in millable polyurethanes because of its high crystallizability. Further, it is generally adopted practice to homo- or copolymerize a long chain diol having a side chain such as a methyl group in order to decrease the concentration of the ester groups and, hence, the crystallizability thereof. For example, use of a homopolymer of 3-methyl-1,5-pentanediol adipate or use of copolyester of hexanediol and neopentyl glycol, no problem of crystallization occurs at low temperatures so that elastomers having excellent hydrolysis resistance can be obtained. However, on the other hand, no sufficient mechanical strength inherent to polyurethanes, such as wear resistance, cannot be obtained. When dibasic acids other than adipic acid are used, the same results are obtained. As described above, the conventional approach for solving the problems of crystallization at low temperatures had resort to randomly disturbing the structural regularity of polyols and therefore when the polymer is deformed excessively the crystallization is prevented so that orientation crystallization tends to occur with difficulty, thus failing to give sufficient mechanical strengths that polyurethanes have inherently.

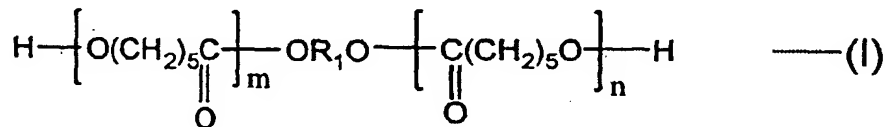
SUMMARY OF THE INVENTION

Under the circumstances, an object of the present invention is to provide a method for producing a polyester based millable polyurethane which method can give rise to a polyurethane that has excellent hydrolysis resistance, shows no crystallization at low temperatures as well as has excellent mechanical properties such as wear resistance.

The present invention provides the following:

1) A method for producing a millable polyurethane, comprising the steps of:

producing a poly-ε-caprolactone based diol represented by formula (I)



wherein $[\]$ is a caprolactone unit; m and n are numbers of caprolactone units; and R_1 is a divalent group derived from a polymerization initiator of formula $R_1(\text{OH})_2$, the poly-ε-caprolactone based diol containing a controlled average number of caprolactone units and having a molecular weight distribution M_w/M_n of 1.0 to 1.5; and

reacting the poly-ε-caprolactone based diol with a diisocyanate to produce a polyurethane with a restricted crystallizability having entropy elasticity.

2) The method for producing a millable polyurethane as described in 2) above, wherein the molecular weight distribution M_w/M_n of the poly-ε-caprolactone based diol is 1.0 to 1.3.

3) The method for producing a millable polyurethane as described in 1) or 2) above, wherein a polymerization initiator represented by formula, $R_1(\text{OH})_2$, for the poly-ε-caprolactone based diol is at least one member selected from the group consisting of straight chain glycols having 2 to 12 carbon atoms; diols having a containing up to 12 carbon atoms and having a side chain, such as neopentyl glycol, 3-methyl-1,5-pentanediol; and diols having an unsaturated group containing up to 12 carbon atoms, such as 3-allyloxy-1,2-propanediol, and wherein the caprolactone unit is present in an average number of 3 to 6.

4) The method for producing a millable polyurethane as described in 3) above, wherein the polymerization initiator, $R_1(\text{OH})_2$, is at least one member selected from the group consisting of straight chain glycols having 2 to 12 carbon atoms, the glycols having no side chain.

5) The method for producing a millable polyurethane as described in 1) or 2) above, wherein the polymerization initiator, $R_1(\text{OH})_2$, is at least one member selected from the group consisting of diols having an aromatic ring, such as 1,4-bis(hydroxyethoxy)benzene and p-xylene glycol; and alicyclic diols, such as cyclohexanediol and cyclohexanedimethanol, and wherein the caprolactone unit is present in an average number of 4 to 8.

6) The method for producing a millable polyurethane as described in any one of 1) to 5) above, the polyol further comprises a chain extender.

7) The method for producing a millable polyurethane as described in any one of 1) to 6) above, wherein the millable polyurethane has a glass transition temperature, T_g , of no higher than -20°C .

8) The method for producing a millable polyurethane as described in any one of 1) to 7) above, wherein the diisocyanate is at least one member selected from the group consisting of 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), and 3,3-dimethyldiphenyl-4,4'-diisocyanate (TODI).

9) The method for producing a millable polyurethane as described in any one of 1) to 8), wherein the poly-ε-caprolactone based diol is prepared under conditions of no higher than 130°C using a tin catalyst represented by formula (II)



wherein R_2 is a hydrogen atom, an alkyl group, or an aryl group; and X is a hydroxyl group, an alkoxide group or a

halogen atom other than fluoride.

10) A method for producing a polyurethane elastomer, comprising the steps:

producing a millable polyurethane according to the method described in any one of 1) to 9) above; and crosslinking the millable polyurethane with a curing agent and molding the resulting cured polyurethane to form a polyurethane elastomer.

11) The method for producing a polyurethane elastomer as described in 10) above, wherein the curing agent is at least one member selected from the group consisting of organic peroxides, sulfur, organic nitrogen-containing compounds, and isocyanate compounds. The polyurethane of the present invention is a millable polyurethane which can be prepared using conventional generally used rubber processing installment, but because of containing the specified polyol, which includes as a main component poly- ϵ -caprolactone based diol, the average number of whose ϵ -caprolactone units is within a predetermined range, the molecular weight distribution, Mw/Mn, of which is does not cause crystallization at low temperatures so that it exhibits excellent mechanical strength and improved hydrolysis resistance.

12) A polyurethane molded article comprising a mixture of a millable polyurethane prepared by a method as described in any one of 1) to 9) above and a curing agent, the mixture being crosslinked and molded.

13) The polyurethane molded article as described in 12) above, wherein the curing agent is at least one member selected from the group consisting of organic peroxides, sulfur, organic nitrogen-containing compounds, and isocyanate compounds.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a diagram illustrating temperature dependence of ball rebound;

Fig. 2 is a diagram illustrating results of DSC measurement of Example 3;

Fig. 3 is a diagram illustrating results of DSC measurement of Comparative Example 7;

Fig. 4 is a diagram illustrating results of DSC measurement of Example 4;

Fig. 5 is a diagram illustrating results of DSC measurement of Comparative Example 8;

Fig. 6 is a diagram illustrating results of DSC measurement of natural rubber;

Fig. 7 is a diagram illustrating results of WAXD measurement of Example 3;

Fig. 8 is a diagram illustrating results of WAXD measurement of Comparative Example 7;

Fig. 9 is a diagram illustrating results of WAXD measurement of Example 4;

Fig. 10 is a diagram illustrating results of WAXD measurement of Comparative Example 8; and

Fig. 11 is a diagram illustrating results of hydrolyzability tests.

DETAILED DESCRIPTION OF THE INVENTION

The method of the present invention, unlike the conventional methods, controls the number and molecular weight distribution of caprolactone units, thereby making it possible to design polyurethane chains using ϵ -caprolactone, which is a monomer having too strong a crystallizability for it to be used in conventional methods. Accordingly, the present invention increases freedom to obtain polyurethanes having desired properties. More specifically, controlling the average number and molecular weight distribution of caprolactone units prevents the crystallization of ϵ -caprolactone due to the influence of a connecting part which is connected to the ϵ -caprolactone. Here, the connecting part comprises a moiety derived from the initiator for ring-opening polyurethanes thus prepared preferably have a glass transition temperature of no higher than -20°C in order for them to be useful as an elastomer when used alone. As is well known in the art, addition of plasticizers or other components and the like to the polyurethanes decreases their Tg substantially so that they can be used more suited for the purposes.

The method of the present invention enables one to control the average number and molecular weight distribution of caprolactone units in crystallizable oligomer comprising ϵ -caprolactone monomers, which in turn controls the crystallizability and amorphous property of the resulting polyurethane reversibly. As a result, it is possible to prepare high performance or high functional elastomers that act as an entropy elastic body in the deformation condition under normal environment because of prevention of crystallization whereas exhibit crystallizability under excessive deformation conditions.

Note that polyurethanes comprising a polycaprolactone based polyol having a narrow molecular weight distribution is disclosed in, for example, Examined Published Japanese Patent Application (Kokoku) No. 39007/1988. This is intended to develop polyurethanes having improved recovery of elasticity. Polyols having narrow molecular weight distributions are disclosed in Examined Published Japanese Patent Application (Kokoku) No. 56251/1991, Unexamined Published Japanese Patent Application (Kokai) No. 292083/1995, and Unexamined Published Japanese Patent Application (Kokai) No. 196623/1988, respectively. They are intended to provide new polyols.

Heretofore, to the inventors' knowledge, there has been no idea of controlling, for example, the molecular weight and molecular weight distribution of polyol within an appropriate range before reaction with diisocyanate to control the crystallizability of the polyol for millable polyurethanes.

The present invention is based on the discovery that concerning poly- ϵ -caprolactone based polyols, presence of ϵ -caprolactone units more than is predetermined results in crystallization of the part concerned and that increase in the number of molecules having a molecular weight not larger than a predetermined molecular weight causes failure to decrease the glass transition temperature, T_g , of the polyurethane so that no desirable entropy elasticity can be obtained.

According to the method of the present invention, there occurs no decrease in mechanical properties such as wear resistance unlike the conventional methods in which use is made of monomers having a side chain such as a methyl group for copolymerization in order to decrease the crystallizability of the resulting polymer. The advantage of the method of the present invention is believed to be attributable to their capability of more speedy crystallization when the polyurethanes are drawn or stretched.

More specifically, in the method of the present invention, the crystallizability of crystallizable monomers can be controlled and hydrolysis resistance can be improved using initiators having no side chain such as a methyl group. In other words, use of initiators having no side chain can improve not only the hydrolysis resistance but also mechanical properties of the resulting polyester based polyurethane. Even when initiators with side chains are used, though mechanical properties are lower than those obtained using initiators having no side chain, there can be obtained millable polyurethanes containing ϵ -caprolactone units with excellent hydrolysis resistance.

The millable polyurethane used in the present invention can be obtained by the reaction between a long chain polyol and a diisocyanate.

As for the polyol to be used in the present invention, poly- ϵ -caprolactone based diol is used as a main component. The poly- ϵ -caprolactone based diol means a product of ring-opening polymerization of ϵ -caprolactone in the presence of a polymerization initiator having active hydrogen atoms and represented by the formula (I) above, among which, there is used in the present invention very limited ones such that the average number of caprolactone units (i.e., average values of m and n as described below) is within a predetermined range, and the molecular weight distribution, M_w/M_n , of the caprolactone unit moiety is 1.0 to 1.5, preferably 1.0 to 1.3.

The reason why the average number of caprolactone units in the poly- ϵ -caprolactone based diol to be used in the present invention is limited within the predetermined range, for example, 3 to 6 is that in the millable polyurethane of the present invention comprising a caprolactone unit and a polyurethane linkage, the caprolactone unit maintains reversible conditions such that under conditions where no strong stress is applied becomes amorphous under the influences of the urethane linkages derived from diisocyanate and R_1 in the above formula so that the caprolactone unit as a whole maintains the amorphous state to show elasticity while in a non-ordinary state where the poly- ϵ -caprolactone unit is subjected to a force such as tensile force and is going to ruin, the poly- ϵ -caprolactone unit exhibits its inherent orientation crystallizability, and contributes to the strength of the polyurethane. Also, the molecular weight distribution, M_w/M_n , of the caprolactone unit is set up to 1.0 to 1.5, preferably 1.0 to 1.3 in order to limit the amount of the molecules outside the upper limit of the predetermined range of the number of caprolactone units. That is, if the number of caprolactone units is greater than 6 or 8, for example, which may vary depending on R_1 , the caprolactone units tend to crystallize under stress, particularly when stored at low and normal temperatures, and once the crystallization starts in this 6-or 8-caprolactone unit, those portions having 3 to 6 or 4 to 8 caprolactone units will also crystallize with ease. The crystallization at low temperatures is a serious damage to the viscoelasticity, high friction coefficient and the like functions of the polyurethane as an elastomer substantially and is disadvantageous in that the environments of use and storage of the polyurethane are restricted greatly.

On the other hand, with smaller number of the caprolactone units than the predetermined number, T_g increases so that the polyurethanes can have no sufficient entropy elasticity in order for it to be useful as an elastomer. The range where no acceptable rubber-like elasticity is exhibited depends on the type of R_1 in the above-described formula and the number of unit of 2 or less is undesirable when R_1 is derived from, for example, aliphatic diols and the number of unit of 3 or less is undesirable when R_1 is derived from, for example, diols having aromatic rings. The T_g of the elastomer can be adjusted by addition of plasticizers and the like and, hence, shorter repeating units can be selected depending on the purposes.

Unexamined Published Japanese Patent Application (Kokai) No. 628/1990, for example, discloses lactone polymers having narrow molecular weight distributions and suggests usefulness of such lactone polymers as a raw material for polyurethanes. However, the prior art described above is intended to lower the viscosity of the lactone polymer to improve its handling property but fails to suggest the method of the present invention. Furthermore, the description in the publication that the lactone polymer is useful as a raw material for polyurethanes, considered based on the state of the art at that time, means that it can be used as a raw material for castable polyurethanes and thermoplastic polyurethanes. The method for preparing lactones having a narrow molecular weight distribution disclosed in Unexamined Published Japanese Patent Application (Kokai) No. 196623/1988 aims at obtaining effects similar to that as above and suggests the present invention in no way.

That is, while high crystallizability raw materials such as ϵ -caprolactone polymers has been considered to be usable as polyol raw material for castable or thermoplastic polyurethanes comprising a hard segment made of an isocyanate and a chain extender and a polyol soft segment, it has been considered that no high crystallizability raw material can be used for millable polyurethanes comprising polyols extended by isocyanates and that there can be used only those polyols that have low crystallizability as a result of introduction of branching chains or comonomers. Accordingly, one skilled in the art does not come up to means for embodying the idea of using the high crystallizability lactone polymer as a raw material for producing millable polyurethanes on practically acceptable grades taking into consideration of prolonged use at low temperatures. Actually, the polyol raw material conventionally used for millable polyurethanes includes only a limited members of polyols such as ethylene propylene glycol adipate and ethylene butylene adipate.

The present invention destroys the conventional technical common sense and as described above controls the number of units in the caprolactone unit, thereby preventing the crystallization of the unit of poly- ϵ -caprolactone based polyol which inherently has a high crystallizability by means of the isocyanate units constituting the urethane linkages and the R_1 moiety in the formula described above and giving a millable polyurethane having an elasticity.

In the present invention, the polymerization initiator for forming the poly- ϵ -caprolactone based polyol, i.e., the original compound for constituting the above-described R_1 is not limited particularly and any compounds may be used as far as they have one or more active hydrogen atoms and form one or more diols after ring-open polymerization. Diols and diamines can be used for the purpose. However, in order to more remarkably exhibit the effects of the present invention, it is preferred to use those which have no molecular weight distribution, i.e., short chain polymerization initiators. The poly- ϵ -caprolactone based polyols formed with such short chain polymerization initiators can be defined, for example, as those having a molecular weight of R_1 of no greater than 500. Alternatively, they can also be defined as those having a total molecular weight of poly- ϵ -caprolactone based polyol of 800 to 1,500.

Such an initiator gives an influence on the crystallizability of the caprolactone unit as described above. Therefore, in the case where R_1 is a straight chain hydrocarbon, for example, the above-described average number of the caprolactone unit must be controlled to 3 to 6. For example, when R_1 is derived from an initiator having high steric hindrance such as an aromatic ring, an aliphatic ring, etc., the caprolactone unit, the average number of the caprolactone units may be controlled to 4 to 8. That is, in the method of the present invention, the average number of the caprolactone units is controlled to a predetermined number depending on the type of the polymerization initiator.

Examples of the short chain initiators which can be used in the present invention include straight chain glycols having 2 to 12 carbon atoms in the main chain thereof, such as ethylene glycol, 1,3-propylene glycol, and 1,4-butylene glycol; diols having a side chain and having up to 12 carbon atoms, such as neopentyl glycol and 3-methyl-1,5-pentanediol; diols having an unsaturated group and having up to 20 carbon atoms, such as 3-allyloxy-1,2-propanediol; and diols having an aromatic ring and having up to 12 carbon atoms, such as 1,4-bis(hydroxyethoxy)benzene and p-xylene glycol; alicyclic diols such as cyclohexanediol and cyclohexanemethanol; and the like. These short chain initiators may be used singly or two or more of them may be used in combination.

For producing poly- ϵ -caprolactone based polyols which are used in the present invention, selection of catalysts as well as ϵ -caprolactone and polymerization initiator is important. As the catalyst which can control the molecular weight distribution of polyol to narrow ranges, there can preferably be used metal compound catalysts containing halogens or organic acid radicals, for example, tin dihalides such as chloride, bromide, iodide, etc. and the tin based catalyst represented by the formula (II) above.

In preparing the poly- ϵ -caprolactone based polyols with a narrow molecular weight distribution, which are used advantageously in the present invention, it is preferred to polymerize the corresponding ϵ -caprolactone monomers at low temperatures as low as, preferably, 130°C or below for a sufficient time using the tin based catalyst represented by formula (II) above, for example, monobutyltin oxide or tin halides excepting tin fluoride. In this manner, use of monobutyltin oxide or tin halides (excluding fluoride) can give rise to a mono-disperse poly- ϵ -caprolactones having a molecular weight distribution within the range of 1.0 to 1.3 even at temperatures within the range of 100 to 200°C with a minimized possibility that crystallization occurs according as the polymerization reaction proceeds, thus allowing practicing the reaction in the absence of solvents. On the contrary, the technique described in Unexamined Published Japanese Patent Application (Kokai) No. 196623/1988 polymerizes lactone by ring opening polymerization reaction with an inorganic acid catalyst at a temperature of 100°C or lower instead of 100°C to 200°C used in the preceding techniques to give highly mono-disperse lactone polymers having a molecular weight distribution within the range of 1.0 to 1.2. In the case of bulk polymerization reactions at such low temperatures, crystallization tends to occur according as the polymerization reaction proceeds so that it has been recommended to perform the reaction in the presence of inert organic solvents such as benzene and toluene. However, this requires an additional step of removing or recovering solvents from the reaction mixture after completion of the reaction, which could be a bar to perform the reaction on an industrial scale.

In the present invention, the above-described specified poly- ϵ -caprolactone based diol, which is a long chain polyol, is used as a main component of the polyol and in addition thereto a long chain polyol and chain extenders generally used can be employed in amounts within the range where the object of the present invention is not harmed. As the generally used long chain polyols, there can be used either polyester polyols or polyether polyols, or blends copolymeriza-

tion products or partially modified products therefrom. Examples of the chain extenders include straight chain glycols having 2 to 12 carbon atoms in the main chain, such as ethylene glycol, thiodiethanol, propylene glycol, and butylene glycol; diols having an aromatic ring and having up to 20 carbon atoms, such as 1,4-bis(hydroxyethoxy)benzene and p-xylene glycol and hydrogenated products thereof. Additionally, triols such as trimethylol; or stearyl alcohol, hydroxyethyl acrylate, and the like can also be used.

In the case where the polyurethane obtained by the method of the present invention is crosslinked with sulfur, a compound having an unsaturated bond is used as a part of the polymerization initiator or chain extender in accordance with conventional manner.

The polyisocyanates which are reacted with such the above-described polyol for producing the polyurethane of the present invention includes 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), 3,3-dimethyldiphenyl-4,4'-diisocyanate (TODI), and the like. Use of 4,4'-diphenylmethane diisocyanate (MDI) is particularly preferred since it is known to act as a crosslinking site for crosslinking with peroxides.

Blend proportion of polyol to diisocyanate may be within generally used ranges. For example, active hydrogen such as hydroxyl group in the diol and isocyanate are blended in equimolar amounts. More specifically, for example, 25 parts by weight of MDI per 100 parts by weight of the diol is used for a hydroxyl number (OHv: KOHmg/g) of 112, 20.8 parts by weight of MDI per 100 parts by weight of diol for OHv of 94, 16.7 parts by weight of MDI per 100 parts by weight of diol for OHv of 75.

The millable polyurethane of the present invention is kneaded with a curing agent and heat cured (crosslinked). Examples of such a curing agent include organic peroxides, sulfur, organic sulfur-containing compounds, isocyanates, and the like for ordinary synthetic rubbers. In the present invention, generally, organic peroxides are used. Examples of the organic peroxides include dicumyl peroxide, a,a'-bis(t-butylperoxyisopropyl)benzene, and the like. The amount of the organic peroxide to be added is on the level of 0.5 to 10 parts by weight, preferably 1.5 to 5 parts by weight, per 100 parts by weight of combined polyol and isocyanate. It is in the case where the polymerization initiator or chain extender has an unsaturated bond, such as 3-allyl-1,2-propanediol, that sulfur and organic sulfur containing compounds can be used as a curing agent. Examples of the organic sulfur-containing compounds include thiuram based vulcanization promoters such as tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide (TETD), and dipentamethylenethiuram tetrasulfide (DPTT), 4,4'-dithiomorpholine, and the like.

Upon kneading and curing as described above, commonly used additives, i.e., reinforcing materials such as carbon black, silica, etc., detackifiers such as wax, plasticizers such as dioctyl phthalate (DOP) can be used.

The polyurethane of the present invention may contain a hydrolysis preventing agent such as polycarbodiimide in amounts of about 0.2 to 3 parts by weight per 100 parts by weight of the polyurethane in the same manner as in conventional methods. The polyurethane member of the present invention has an improved hydrolysis resistance twice or more as high as the conventional thermosetting millable polyurethanes and use of hydrolysis preventing agents in the polyurethane of the present invention in the same amount as the conventional polyurethanes the hydrolysis resistance of the polyurethane material of the present invention is increased accordingly while in order to obtain the same level of hydrolysis resistance as the conventional polyurethane materials, the amount of the additive to be added can be reduced by about 20% to 50% of the amount of the conventional additive. This contributes much to reduction in costs since the hydrolysis preventing agents are generally expensive.

The millable polyurethane of the present invention can be reacted under the conditions of generally 70°C to 150°C for 30 to 10 hours and thereafter aged if necessary at 40°C to 120°C for about 6 to 48 hours. The heat curing conditions of the millable polyurethane may be determined depending on the decomposition properties of the organic peroxide to be used but generally it is preferred that the heat curing conditions are set within the range of 150 to 180°C for 3 to 60 minutes.

DESCRIPTION OF PREFERRED EMBODIMENTS

Hereafter, the present invention will be described in greater detail by embodiments.

Hereafter, the present invention will be described in greater detail by embodiments.

Production Example 1: Production of Poly-ε-Caprolactone Based Diols

Ethylene glycol as a polymerization initiator and ε-caprolactone in respective amounts shown in Table 1 were reacted in the presence of SnCl₂ or TBT as a catalyst to prepare various poly-ε-caprolactone based diols.

Here, the diols of the group of Examples 1 to 4 and A) had a molecular weight distribution as narrow as about 1.4 while the diols of the group of Comparative Examples 4 to 10 (hereafter, referred to as Group B) had a molecular weight distribution of about 2.2, which value was within the range usually used in the conventional techniques. Table 1 shows the amount of catalyst and reaction temperature used in each reaction, the designed and calculated values of the number of ε-caprolactone units, designed and found values of average molecular weight, and molecular weight distribution.

bution (Mw/Mn).

Here, the average molecular weights were determined by measuring the hydroxyl number of polyols according to JIS K1557-6.4 and calculating by the following equation:

$$\text{Molecular Weight} = 56.1 \times N \times 1000 / \text{Hydroxyl Number}$$

where N is the number of functional groups in the polymerization initiator.

Further, the molecular weight distribution was determined by gel permeation chromatography (GPC) under the following conditions:

Apparatus: LC-3A, SHIMAZU SEISAKUSHO;
 Solvent: Tetrahydrofuran (1ml/min.)
 Temperature: 50°C
 Column: Shodex KF801 1 tube
 KF8025 1 tube
 KF804 1 tube
 Detector: RID-6A, SHIMAZU SEISAKUSHO

Table 1

Ex	C-Ex	Ini.		ϵ -CL	CAT		R.Temp	NCL	AMW	AMW	ALN	Mw/Mn
		K.	P.	P.	K.	ppm	°C	Dd.	Dd.	Md.	Cd.	
A	1	EG	62	570	SnCl ₂	5	150	2.5	632	616	2.4	1.4
	2	EG	62	684	SnCl ₂	5	150	3	746	810	3.3	1.4
	3	EG	62	912	SnCl ₂	5	150	4	974	999	4.1	1.3
	4	EG	62	1140	SnCl ₂	5	150	5	1202	1163	4.8	1.4
	5	EG	62	1368	SnCl ₂	5	150	6	1430	1480	6.2	1.3
	6	EG	62	1596	SnCl ₂	5	150	7	1658	1647	7.0	1.4
	7	EG	62	1938	SnCl ₂	5	150	8.5	2000	1991	8.5	1.4
B	8	EG	62	570	TBT	10	170	2.5	632	641	2.5	2.3
	9	EG	62	684	TBT	10	170	3	746	792	3.2	2.2
	10	EG	62	912	TBT	10	170	4	974	974	4.0	2.1
	11	EG	62	1140	TBT	10	170	5	1202	1184	4.9	2.3
	12	EG	62	1368	TBT	10	170	6	1430	1460	6.1	2.1
	13	EG	62	1596	TBT	10	170	7	1658	1699	7.2	2.2
	14	EG	62	1938	TBT	10	170	8.5	2000	1991	8.5	2.3

Ex.: Example, C-Ex.: Comparative Example

Ini.: Initiator, K.: Kinds, P.: Parts,

ϵ -CL: ϵ -caprolactone, P.: Parts

CAT: Catalyst, K.: Kinds

R.Temp: Room Temperature

NCL(Dd.): Designed values of the number of ϵ -caprolactone units,

AMW(Dd.): Designed values of average molecular weight

AMW(Md.): Measured values of average molecular weight

NCL(Cd.): Calculated values of the number of ϵ -caprolactone units

Production Example 2: Production of Millable Polyurethane

Each of the poly- ϵ -caprolactone based polyols and equimolar amount of 4,4'-diphenylmethane diisocyanate (MDI) were reacted at 100°C for 5 hours to obtain various millable polyurethanes.

In order to evaluate the properties of the millable polyurethanes thus obtained as an amorphous polymer chain their glass transition temperature, T_g, and the stability during storage at low temperatures was examined. The stability during storage at low temperatures was judged from their flexibility at temperatures of -15°C, 5°C and 25°C. Table 2 shows the results obtained.

As a result, it was observed that in both group A having a narrower molecular weight distribution and group B having a broader molecular weight distribution, the crystallizability of the polyurethanes increased with an increased average number of ϵ -caprolactone units. Group A had a wider temperature range than group B at which the amorphous state can be maintained.

Table 2

	Ex	C-Ex	Ini.	NCI	Mw/Mn	T _g	Properties of GUM		
							(Prop. after 3days)		
							-15°C	5°C	25°C
A		1	EG	2.4	1.4	-10	Am	Am	Am
	1		EG	3.3	1.4	-24	Am	Am	Am
	2		EG	4.1	1.3	-33	Am	Am	Am
	3		EG	4.8	1.4	-37	Cry	Am	Am
	4		EG	6.2	1.3	-41	Cry	Cry	Am
		2	EG	7.0	1.4	-45	Cry	Cry	Cry
		3	EG	8.5	1.4	-48	Cry	Cry	Cry
B		4	EG	2.5	2.3	-12	Am	Am	Am
		5	EG	3.2	2.2	-24	Am	Am	Am
		6	EG	4.0	2.1	-34	Cry	Am	Am
		7	EG	4.9	2.3	-38	Cry	Cry	Am
		8	EG	6.1	2.1	-42	Cry	Cry	Cry
		9	EG	7.2	2.2	-46	Cry	Cry	Cry
		10	EG	8.5	2.3	-48	Cry	Cry	Cry

Ex.: Example, C-Ex.: Comparative Example

Ini.: Initiator, K.: Kinds, P.: Parts,

T_g: Glass transition temperature

NCI(Dd.): Designed values of the number of ϵ -caprolactone units,

Properties of GUM: Properties of polyurethane

Prop. After 3 days: Properties after standing at each temp. for 3 days

Am: Amorphous

Cry: Crystallization

Production Example 3: Production of Crosslinked Polyurethane

To 100 parts by weight of each of the millable polyurethanes produced as described above was added 1.5 parts by weight of dicumyl peroxide (NIPPON FATS & OIL; PERCUMYL D (trade name)) and the mixture was kneaded in an open roll and press-molded at 160°C for 20 minutes to obtain various crosslinked elastomers.

Measurement of Physical Properties

These crosslinked elastomers were measured for hardness (Hs: JIS A scale) according to JIS K6253, ball rebound (Rb: %) according to JIS K6255 (based on ISO 4662), tensile strength (Tb: MPa) and elongation (Eb: %) according to JIS K6251 (based on ISO 37), tear strength using a notched, an angled test piece (Tr: N/mm) according to JIS K6252 (based on ISO 34). Table 3 shows the results obtained. Further, the crosslinked elastomers were also measured for hardness after standing at various temperatures for 3 days. Table 3 also shows the results of these tests. Furthermore, Samples 3, 4, 9, and 10 were measured for temperature dependence of ball rebound at -20°C to 60°C. Fig. 1 illustrates the results.

Each crosslinked elastomer was observed for the phenomenon of "cold hardening", i.e., an increase in hardness from the hardness after standing at various temperature for 3 days due to crystallization. Then, the elastomers produced using poly-ε-caprolactone having a molecular weight of 1,500 (average number of units of 6) suitable for use in conventional castable elastomers showed an increase in hardness even at temperatures near normal temperature. In those elastomers that were produced using poly-ε-caprolactone units of 3 or less showed no crystallizability but temperature dependence of the physical properties of the elastomer increases unacceptably at around normal temperature so that the resulting elastomer is unsuitable. On the other hand, use of poly-ε-caprolactone gave rise to elastomers which are less dependent on temperature without increasing the hardness.

These facts suggest that an increase in hardness due to crystallization is considered to depend on the number of lactone monomer units and on the contrary, the number of units exceeds a predetermined value, the crystallizability of the polymer increases too high for the polymer to be suitable as an amorphous polymer chain in elastomers. When the average number of monomer units is below a predetermined value (e.g., below 3), the concentration of urethane group in the amorphous polymer chain increases so that the glass transition temperature of the polymer chain increases and gives an adverse influence on the temperature dependence. Therefore, in order for the elastomers to have low glass transition temperatures sufficient for practical purposes (e.g., -20°C or below) while prevented from crystallizing, it is useful to highly control the molecular weight distribution of poly-ε-caprolactone. Further, based on the knowledge that what is crystallized is the poly-ε-caprolactone unit, it is considered possible to finely control the crystallizability of the poly-ε-caprolactone unit, which was impossible by the conventional techniques, by selectively arranging molecules that control the crystallization of the linkage unit at both ends thereof.

Table 3

			Property of Elastomers								
	Ex	C-Ex						Hs (after 3days)			
			Hs	Rb	Tb	Eb	Tr	-20°C	0°C	10°C	20°C
A		1	53	48	12.8	560	23.7	95	55	52	50
	1		53	60	18.5	520	25.8	54	54	53	53
	2		53	66	19.2	520	23.7	52	53	53	53
	3		52	72	17.4	510	28.6	65	54	54	53
	4		53	69	18.5	510	38.5	85	92	92	52
		2	54	71	24.1	520	49.8	94	93	93	85
		3	55	73	24.8	520	57.7	94	93	93	87
B		4	54	52	15.3	540	25.1	90	55	54	53
		5	49	60	18.8	520	23.6	55	54	49	49
		6	48	66	20.2	510	31.5	85	87	52	47
		7	53	72	19.3	540	28.3	85	89	88	53
		8	54	74	23.1	510	41.7	91	93	93	79
		9	92	65	24.2	520	44.2	95	95	94	94
		10	93	65	23.8	550	57.7	96	95	94	94
Ex.: Example, C-Ex.: Comparative Example											
Hs(after 3 days): Hardness after standing at various temperature for 3 days											

Production Example 4: Production of Poly- ϵ -Caprolactone Based Diol

Ethylene glycol as a polymerization initiator and ϵ -caprolactone in respective amounts shown in Table 5 were reacted using various amounts of catalyst and at various temperatures to prepare various poly- ϵ -caprolactone based diols.

Here, the diols of the group of Examples 5 to 7 and Comparative Examples 11 and 12 (hereafter, referred to as Group C) had a fixed average number of ϵ -caprolactone units of 6 and a varied molecular weight distribution within the range of 1.15 to 2.13 while the diols of the group of Examples 8 to 10 and Comparative Examples 13 and 14 (hereafter, referred to as Group D) had a fixed average number of ϵ -caprolactone units of 5 and a varied molecular weight distribution within the range of 1.18 to 2.21. Table 4 shows the amount of catalyst and reaction temperature used in each reaction, the designed and calculated values of the number of ϵ -caprolactone units, designed and found values of average molecular weight, and molecular weight distribution (Mw/Mn).

Table 4

	Ex	C-Ex	Ini.		ϵ -CL P.	CAT		R.Temp °C	NCI Dd.	AMW		NCI Cd.	Mw/Mn
			K.	P.		K.	ppm			Dd.	Md.		
C		11	EG	62	1368	TBT	10	170	6	1430	1457	6.1	2.13
		12	EG	62	1368	SnCl ₂	5	170	6	1430	1414	5.9	1.86
	5		EG	62	1368	SnCl ₂	5	150	6	1430	1407	5.9	1.45
	6		EG	62	1368	MBTO	50	150	6	1430	1478	6.2	1.29
	7		EG	62	1368	MBTO	50	120	6	1430	1451	6.1	1.15
D		13	EG	62	1140	TBT	10	170	5	1202	1211	5.0	2.21
		14	EG	62	1140	SnCl ₂	5	170	5	1202	1238	5.2	1.83
	8		EG	62	1140	SnCl ₂	5	150	5	1202	1216	5.1	1.41
	9		EG	62	1140	MBTO	50	150	5	1202	1254	5.2	1.28
	10		EG	62	1140	MBTO	50	120	5	1202	1170	4.9	1.18
Ex.: Example, C-Ex.: Comparative Example Ini.: Initiator, K.: Kinds, P.: Parts, ϵ -CL: ϵ -caprolactone, P.: Parts CAT: Catalyst, K.: Kinds R.Temp: Room Temperature NCI(Dd.): Designed values of the number of ϵ -caprolactone units, AMW(Dd.): Designed values of average molecular weight AMW(Md.): Measured values of average molecular weight NCI(Cd.): Calculated values of the number of ϵ -caprolactone units													

Production Example 5: Production of Millable Polyurethane

In the same manner as in Production Example 1 above, each of the poly- ϵ -caprolactone based polyols and equimolar amount of 4,4'-diphenylmethane diisocyanate (MDI) were reacted at 100°C for 5 hours to obtain various millable polyurethanes.

In order to evaluate the properties of the millable polyurethanes thus obtained as an amorphous polymer chain their glass transition temperature, T_g, was measured and also evaluate the stability during storage at low temperatures, their crystallizability was judged from their flexibility at temperatures of -15°C, 5°C and 25°C. Table 5 shows the results obtained.

Table 5

	Ex	C-Ex	Properties of GUM						
			Ini.	NCI	Mw/Mn	Tg	Prop. (after 3days)		
			K.	(Cd.)		°C	-15°C	5°C	25°C
C		11	EG	6.1	2.13	-42	Cry	Cry	Cry
		12	EG	5.9	1.86	-42	Cry	Cry	Cry
	5		EG	5.9	1.45	-41	Cry	Cry	Am
	6		EG	6.2	1.29	-41	Cry	Cry	Am
	7		EG	6.1	1.15	-41	Cry	Cry	Am
D		13	EG	5.0	2.21	-38	Cry	Cry	Am
		14	EG	5.2	1.83	-39	Cry	Cry	Am
	8		EG	5.1	1.41	-37	Cry	Am	Am
	9		EG	5.2	1.28	-37	Am	Am	Am
	10		EG	4.9	1.18	-37	Am	Am	Am
Ex.: Example, C-Ex.: Comparative Example Ini.: Initiator, K.: Kinds, P.: Parts, Tg: Glass transition temperature NCI(Dd.): Designed values of the number of ϵ -caprolactone units, Properties of GUM: Properties of polyurethane Prop. After 3 days: Properties after standing at each temp. for 3 days Am: Amorphous Cry: Crystallization									

Production Example 6: Production of Crosslinked Polyurethane

Various crosslinked polyurethanes were prepared in the same manner as described in Production Example 1 from the millable polyurethanes produced as described in Production Example 2. Each of the crosslinked polyurethanes was measured for physical properties as described above. Table 6 shows the results obtained.

The change in hardness of the crosslinked polyurethanes indicated that the molecular weight distribution of poly- ϵ -caprolactone based diol, raw material, gave a considerable influence on an increase in hardness due to a decreased crystallization at low temperatures (cold hardening) of elastomers and use of polyols having a very narrow molecular weight distribution made it possible to provide millable elastomers having controlled low temperature crystallizability. The present invention attained maximal effects by the use of polyols similar to mono-disperse polyols as having a molecular weight distribution of 1.5 or less, preferably 1.3 or less, which indicates distribution of caprolactone units. In other words, because the average number of units can be made greater under the conditions where the crystallizability is controlled or limited, it is possible to obtain a glass transition temperature sufficient for practical use as a rubber elastic body so that amorphous elastomers comprising highly crystallizable units that have been contradictory in the prior art can be produced using general purpose production facilities used in rubber industry. Here, the "glass transition sufficient for practical use" may be defined, for example, -20°C. This is because at a glass transition temperature of -20°C or higher, the rubber elasticity observed at normal temperature cannot be maintained at those low temperatures which are encountered ordinarily, such as 0°C.

Table 6

	Ex	C-Ex	Property of Elastomers								
								Hs (after 3days)			
			Hs	Rb	Tb	Eb	Tr	-20°C	0°C	10°C	20°C
C		11	54	74	23.1	510	41.7	91	93	93	79
		12	55	70	21.5	520	39.8	92	94	94	85
	5		53	71	18.5	510	38.5	85	92	92	52
	6		53	72	17.6	500	38.5	85	92	88	52
	7		52	72	18.5	520	36.1	88	90	89	53
D		13	53	72	19.3	540	28.3	85	89	88	53
		14	55	71	16.5	490	25.3	87	90	86	55
	8		52	72	17.4	510	28.6	65	54	54	53
	9		54	70	18.1	520	30.2	54	53	53	54
	10		54	70	17.4	510	28.8	53	54	53	53
Ex.: Example, C-Ex.: Comparative Example											
Hs(after 3 days): Hardness after standing at various temperature for 3 days											

Production Example 7: Production of Poly- ϵ -Caprolactone Based Diol

As shown in Table 9, each of the polymerization initiators selected from 1,4-butanediol (1,4-BD), 1,5-pentanediol (1,5-PD), 1,6-hexanediol (1,6-HD), nonanediol (NP), neopentyl glycol (NPG), 3-methyl-1,5-pentanediol (3MPG), cyclohexanedimethanol (CHDM), p-xylene glycol (PXG), 1,4-bis(hydroxyethoxy)benzene (BHEB), and BPE-20 (SANYO KASEI KOGYO CO., LTD., trade name: an adduct of bisphenol A with 1 mole of ethylene oxide added to each end thereof) was reacted with ϵ -caprolactone under predetermined conditions to prepare poly- ϵ -caprolactone based diols of Examples 11 to 53. For each run, the reaction was proceeded under nitrogen flow and the product was ripen until the remaining caprolactone monomer was reduced to 1% or less as measured by gas chromatography.

Table 7 shows the amount of catalyst and reaction temperature used in each reaction, the designed and calculated values of the number of ϵ -caprolactone units, designed and found values of average molecular weight, and molecular weight distribution (Mw/Mn).

Table 7

Example	Ini.		ε-CL		CAT	R.Temp		AMW	AMW	NCI	Mw/Mn
	K.	P.	P.	K.	ppm	°C	Dd.	Md.	Cd.		
11	1,4-BD	87	913	MBTO	50	120	1000	1017	4.1	1.24	
12	1,4-BD	90	979	MBTO	50	120	1069	1070	4.3	1.20	
13	1,4-BD	90	1140	MBTO	50	120	1230	1206	4.9	1.15	
14	1,4-BD	90	1360	MBTO	50	120	1450	1424	5.9	1.18	
15	1,4-BD	90	1596	MBTO	50	120	1686	1645	6.8	1.17	
16	1,5-PD	104	916	MTBO	50	120	1020	1020	4.0	1.18	
17	1,5-PD	104	1026	MTBO	50	120	1130	1107	4.4	1.18	
18	1,5-PD	104	1140	MTBO	50	120	1244	1228	4.9	1.15	
19	1,5-PD	104	1368	MTBO	50	120	1472	1446	5.9	1.14	
20	1,5-PD	104	1596	MTBO	50	120	1700	1667	6.9	1.19	
21	1,6-HD	118	798	MTBO	50	120	916	923	3.5	1.20	
22	1,6-HD	118	902	MTBO	50	120	1020	1009	3.9	1.18	
23	1,6-HD	118	1140	MTBO	50	120	1258	1243	4.9	1.17	
24	ND	160	860	MTBO	50	120	1020	1012	3.7	1.16	
25	ND	160	1140	MTBO	50	120	1300	1272	4.9	1.15	
26	NPG	104	912	MTBO	50	120	1016	1021	4.0	1.27	
27	NPG	104	1026	MTBO	50	120	1130	1143	4.6	1.31	
28	NPG	104	1140	MTBO	50	120	1244	1240	5.0	1.35	
29	NPG	104	1472	MTBO	50	120	1472	1476	6.0	1.23	
30	NPG	104	1596	MTBO	50	120	1700	1697	7.0	1.23	
31	3-MPD	118	882	MTBO	50	120	1000	1001	3.9	1.24	
32	3-MPD	118	1026	MTBO	50	120	1144	1152	4.5	1.15	
33	3-MPD	118	1140	MTBO	50	120	1258	1271	5.1	1.33	
34	3-MPD	118	1368	MTBO	50	120	1486	1413	5.7	1.18	
35	3-MPD	118	1596	MTBO	50	120	1714	1708	7.0	1.26	
36	CHDM	144	876	MBTO	50	120	1020	1021	3.8	1.18	
37	CHDM	144	1140	MBTO	50	120	1284	1264	4.9	1.15	
38	CHDM	144	1368	MBTO	50	120	1512	1476	5.8	1.16	
39	CHDM	144	1482	MBTO	50	120	1626	1587	6.3	1.14	
40	CHDM	144	1710	MBTO	50	120	1854	1801	7.3	1.15	
41	PXG	138	882	MTBO	50	120	1020	1025	3.9	1.26	
42	PXG	138	1140	MTBO	50	140	1278	1323	5.2	1.21	
43	PXG	138	1368	MTBO	50	140	1506	1556	6.2	1.26	
44	PXG	138	1596	MTBO	50	120	1734	1784	7.2	1.14	
45	PXG	138	1824	MTBO	50	120	1962	2014	8.2	1.15	
46	BHEB	198	1140	MTBO	50	120	1338	1320	4.9	1.15	
47	BHEB	198	1368	MTBO	50	120	1566	1554	5.9	1.16	
48	BHEB	198	1596	MTBO	50	120	1794	1784	7.0	1.14	
49	BHEB	198	1824	MTBO	50	120	2022	2011	8.0	1.14	
50	BPE-20	316	1140	MTBO	50	120	1456	1418	4.8	1.19	
51	BPE-20	316	1368	MTBO	50	120	1684	1662	5.9	1.19	
52	BPE-20	316	1596	MTBO	50	120	1912	1861	6.8	1.18	
53	BPE-20	316	1824	MTBO	50	120	2140	2093	7.8	1.18	

Ini.: Initiator, K.: Kinds, P.: Parts,

ϵ -CL: ϵ -caprolactone, P.: Parts

CAT: Catalyst, K.: Kinds

R.Temp: Room Temperature

NCl(Dd.): Designed values of the number of ϵ -caprolactone units,

AMW(Dd.): Designed values of average molecular weight

AMW(Md.): Measured values of average molecular weight

NCl(Cd.): Calculated values of the number of ϵ -caprolactone units

MBTO: Monobutyl tin oxide

TBT: Tetrabutyl titanate

Production Example 8: Production of Millable Polyurethane

Each of the poly-ε-caprolactone based polyols and equimolar amount of 4,4'-diphenylmethane diisocyanate (MDI) were reacted at 100°C for 5 hours in the same manner as in Production Example 1 above to obtain various millable polyurethanes.

In order to evaluate the properties of the millable polyurethanes thus obtained as an amorphous polymer chain their glass transition temperature, T_g, was measured and also evaluate the stability during storage at low temperatures, their crystallizability was judged from their flexibility at temperatures of -15°C, 5°C and 25°C. Table 5 shows the results obtained. Here, the relative crystallizability was obtained by measuring heat of fusion of a sample using differential scanning calorimeter (DSC) after holding the sample at -10°C for 10 hours and comparing the data with those of natural rubber, followed by rating them based on the following classes: weak (W), medium (M) and strong (S). Table 8 shows the results obtained.

As a result, it revealed that setting simple parameters such as the kind of polymerization initiator and average number of monomer units enables one to finely or precisely control the crystallizability of the amorphous polymer chain in elastomers.

While the crystallizability of crosslinked elastomers can be controlled to some extent by crosslinking or by use of additives, elastomers of the rank "strong" of relative crystallizability are difficult to employ at normal temperature (20°C) since there is the fear that they could cause inconveniences due to crystallizability. Therefore, in the systems using aliphatic diols as a polymerization initiator, the average number of monomer units should be 6 or less. In other words, when the average number of monomer units is 7 or more, crystallization occurs even at room temperature so that the polyurethane cannot be used as a polymer chain in elastomers. Further, if the polymerization initiator has a methyl group as a side chain, crystallization decreases but strength also decreases considerably. On the other hand, introduction of substituents which are bulky in a plane such as a benzene ring and a cyclohexane ring, instead of a methyl group, relaxes crystallizability to a suitable extent while at the same time imparting ability of exhibiting orientation crystallizability when stretched, thereby giving elastomers having high strength. When cyclic structures are introduced in the molecule as described above, the crystallizability is relaxed and therefore polyurethanes with an average number of lactone units of up to about 8 can be used. However, since the introduction of cyclic structures also increases the glass transition temperature of the polymer chain, it is desirable to use polyurethanes with an average number of lactone units of 4 or more in order to have a T_g of -20°C or lower.

Table 8

EX	CAT K.	NCl (Cd.)	Mw/Mn	Tg °C	R. Cry. -10°C
11	1,4-BD	4.1	1.24	-35.8	W
12	1,4-BD	4.3	1.20	-36.5	W
13	1,4-BD	4.9	1.15	-40.5	M
14	1,4-BD	5.9	1.18	-45.3	M-S
15	1,4-BD	6.8	1.17	-48	S
16	1,5-PD	4.0	1.18	-35.2	W
17	1,5-PD	4.4	1.18	-37.2	W
18	1,5-PD	4.9	1.15	-40.1	M
19	1,5-PD	5.9	1.14	-44.2	M-S
20	1,5-PD	6.9	1.19	-46.4	S
21	1,6-HD	3.5	1.20	-31.2	W
22	1,6-HD	3.9	1.19	-33.8	W
23	1,6-HD	4.9	1.17	-40.2	M
24	ND	3.7	1.16	-32.6	W
25	ND	4.9	1.15	-41.3	M
26	NPG	4.0	1.27	-32.8	W
27	NPG	4.6	1.31	-35.3	W
28	NPG	5.0	1.35	-38.9	W
29	NPG	6.0	1.23	-42.6	M-S
30	NPG	7.0	1.23	-45.5	S
31	3-MPD	3.9	1.21	-34.8	W
32	3-MPD	4.5	1.15	-35.2	W
33	3-MPD	5.1	1.33	-38	W
34	3-MPD	5.7	1.18	-39.4	M
35	3-MPD	7.0	1.26	-44	S
36	CHDM	3.8	1.18	-21	W
37	CHDM	4.9	1.15	-34.4	W
38	CHDM	5.8	1.16	-38.8	M
39	CHDM	6.3	1.14	-40.4	M-S
40	CHDM	7.3	1.15	-43.7	M-S
41	PXG	3.9	1.26	-22.2	W
42	PXG	5.2	1.21	-30.3	W
43	PXG	6.2	1.26	-34.9	M
44	PXG	7.2	1.14	-38.4	M-S
45	PXG	8.2	1.15	-41	S
46	BHEB	4.9	1.15	-23.4	W
47	BHEB	5.9	1.16	-28.9	M
48	BHEB	7.0	1.14	-33.2	M-S
49	BHEB	8.0	1.14	-41.2	S
50	BPE-20	4.8	1.19	-22.1	W
51	BPE-20	5.9	1.19	-28.9	W
52	BPE-20	6.8	1.18	-33.8	M
53	BPE-20	7.8	1.18	-41	M-S

CAT: Catalyst, K.: Kinds

NCl (Dd.): Designed values of the number of ε-caprolactone units,

R.Cry.: Relative crystallizability

55 Production Example 9: Production of Crosslinked Polyurethane

Various crosslinked polyurethanes were obtained from the millable polyurethanes of Examples 10, 13, 18, 23, 25, 28, 33, 37, 42, 46, and 50 in the same manner as described above. These crosslinked elastomers were measured for hardness (Hs: JIS A scale) according to JIS K6253, ball rebound (Rb: %) according to JIS K6255 (based on ISO 4662),

tensile strength (Tb: MPa) and elongation (Eb: %) according to JIS K6251 (based on ISO 37), tear strength using a notched, an angled test piece (Tr: N/mm) according to JIS K6252 (based on ISO 34). Table 9 shows the results obtained.

Table 9

Example	Ini.	Polyol m.p.	Hs	Rb	Tb	Eb	Tr
10	EG	37.1, 42.2	54	70	17.4	510	28.8
13	BD	36.8, 39.2	53	72	21.2	520	32.5
18	PD	32.6, 37.5	53	71	15.1	500	26.6
23	HD	36.6, 40.5	54	73	22.8	520	33.5
25	ND	44.1	55	70	20.6	520	30.0
28	NPG	23.2, 34.2	55	69	6.8	430	20.8
33	3-MPD	24.4, 35.7	54	70	7.6	450	22.5
37	CHDM	23.3, 31.1	55	72	18.7	500	32.3
42	PXG	25.6, 36.0	53	70	20.8	520	30.5
46	BHEB	27.2, 35.3	54	68	19.6	530	29.8
50	BPE-20	15.2, 21.3	54	62	18.1	530	36.7

Comparative Tests on Crystallizability

Crystallizability was compared between Group A including Examples 3 and 4 in which the molecular weight distribution of ϵ -caprolactone was narrow and Group B including Comparative Examples 7 and 8 in which the molecular weight distribution of ϵ -caprolactone was broad.

1. Measurement of Crystallizability of Amorphous Polymer Chain Before Crosslinking, Measured Using a Differential Scanning Calorimeter (DSC)

Each sample was measured for the crystallizability of amorphous polymer chain before crosslinking using a differential scanning calorimeter (DSC). Figs. 2 to 5 illustrate the results of DSC measurements on the behavior of fusion of each sample after holding it at -10°C for a predetermined time. For comparison, Fig. 6 shows results of DSC measurement on natural rubber (NR).

It was observed that Comparative Examples 7 and 8 in Group B with a broad molecular weight distribution showed faster crystallization than the samples of Examples 3 and 4 in Group A with a narrow molecular weight distribution. It was observed that the samples with an average number of linkages of 5 were slower in crystallization than the samples with an average number of linkages of 6. From this, it reveals that use of oligomers having a narrow molecular weight distribution enables one to finely control the crystallizability of the amorphous polymer chain by setting a selected average number of linkages.

2. Comparison of Crystallization of Crosslinked Elastomers by Measuring Wide Angle X-ray Diffraction (WAXD)

Each sample was measured for wide angle X-ray diffraction of the amorphous polymer chain. Figs. 7 to 10 illustrate the results of WAXD measurements. Specimens used were each in the form of a 1 mm-thick and 3 mm-wide processed sheet and measurement were conducted at varied elongation (%) at 22°C .

The samples of Comparative Examples 7 and 8 in Group B with a broad molecular weight distribution showed a diffraction peak due to crystallization even when the samples were not stretched. The peak of $2\theta =$ about 21 degree corresponded to the peak position of ϵ -caprolactone and, hence, it is presumed that crystallization due to stretching of the crosslinked elastomers is attributable to the crystallization of the repeating unit of caprolactone monomers.

On the other hand, The samples of Examples 3 and 4 in Group A with a narrow molecular weight distribution were in an amorphous state when they were under the conditions of no or low stretching and from their low glass transition temperature, it is presumed that they can become a rubber elastic body or elastomer. At an increased elongation, crys-

tallization was observed. This indicates that although the samples of the present invention behave as a rubber elastic body under deformation conditions which ordinary elastomers encounter, they are highly oriented and behave similarly to crystallized polymer when they are excessively or drastically deformed as in the case of wear, breakage, or the like. In addition, the degree of crystallization can be finely controlled by adjusting the average number of caprolactone units.

Comparative Examples 15 to 18

There were prepared ethylene glycol butanediol coadipate (EG:BG=1:1) (Comparative Example 15), 3-methyl-1,5-pentanediol adipate (Comparative Example 16), and neopentyl glycol adipate/caprolactone copolymer (NPG/AA:CL=1:2) (Comparative Example 17). Further, commercially available polyester-type millable polyurethane of ethylene glycol butylene coadipate type (SUMIPAN 640S: trade name; SUMITOMO BAYER URETHANE CO., LTD.) was used as Comparative Example 18.

Hydrolyzability Test

The molded products produced from the crosslinked elastomers obtained in Examples 10, 11, 33, 37, and 42 and Comparative Examples 13, and 15 to 18 were measured for changes in hardness (JIS A) when left to stand in water at 85°C. Fig. 11 illustrates the results obtained. Also, the crosslinked elastomers were measured for hardness (Hs: JIS A scale) according to JIS K6253, ball rebound (Rb: %) according to JIS K6255 (based on ISO 4662), tensile strength (Tb: MPa) and elongation (Eb: %) according to JIS K6251 (based on ISO 37), and permanent compression strain (Cs: %) under the conditions of 70°C for 22 hours according to JIS K6262 (based on ISO 815). Table 10 shows the results obtained together with the composition and properties of polyols and the glass transition temperatures of millable polyurethanes.

Table 10

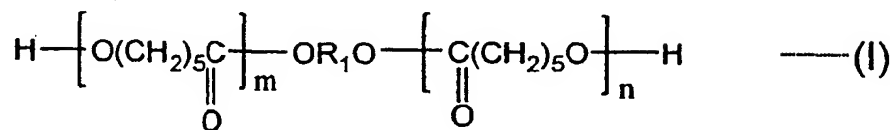
	Polyol Camp.	Property of Polyol GUM				Property of Elastomers					
		Mn	Mw/M n	mp °C	Tvg °C	Hs	Rb	Tb	Eb	Cs	Hs 0°C, 72hr
C-Ex 15	EG:BG/AA	2008	2.3	15	-42	53	68	16.8	530	9	55
C-Ex 16	MPD/AA	2021	2.1	-	-48	52	65	2.7	380	7	53
C-Ex 17	NPG/AA/CL	1990	2.2	2	-49	52	66	3.8	410	7	52
Ex 10	EG/CL	1170	1.18	37, 42	-37	53	68	17.9	520	6	54
C-Ex 13	EG/CL	1211	2.21	42, 46	-38	53	72	19.3	540	7	93
Ex 11	BD/CL	1017	1.24	42, 47	-35	54	73	23.4	520	7	54
Ex 33	MPD/CL	1271	1.33	24, 36	-41	54	74	7.6	450	5	54
Ex 38	CHDM/CL	1476	1.16	28, 34	-36	53	73	18.5	500	8	54
Ex 42	PXG/CL	1323	1.21	26, 36	-30	53	70	20.8	520	8	55
C-Ex 18	SUMIPAN640S				-38	53	67	20.8	580	13	54

These results reveal that the molded products of the Examples using the millable polyurethane of the present invention are superior in hydrolysis resistance over the molded products of the Comparative Examples. While the molded products of Comparative Examples of 16 and 17 had acceptable hydrolysis resistance because of decreased crystallizability as a result of introduction of a methyl group as a side chain, they failed to exhibit high grade of physical properties inherent to polyurethanes because they hardly showed orientation crystallizability when they were stretched. In contrast, the molded articles of the Examples exhibited orientation crystallizability when stretched so that they showed high grade of physical properties inherent to polyurethanes.

Claims

1. A method for producing a millable polyurethane, comprising the steps of:

producing a poly-ε-caprolactone based diol represented by formula (I)



wherein \square is a caprolactone unit; m and n are numbers of caprolactone units; and R_1 is a divalent group derived from a polymerization initiator of formula $\text{R}_1(\text{OH})_2$, the poly-ε-caprolactone based diol containing a controlled average number of caprolactone units and having a molecular weight distribution Mw/Mn of 1.0 to 1.5; and

reacting said poly-ε-caprolactone based diol with a diisocyanate to produce a polyurethane with a restricted crystallizability having entropy elasticity.

2. The method for producing a millable polyurethane as claimed in claim 1, wherein the molecular weight distribution Mw/Mn of said poly-ε-caprolactone based diol is 1.0 to 1.3.
3. The method for producing a millable polyurethane as claimed in claim 1 or 2, wherein a polymerization initiator represented by formula, $\text{R}_1(\text{OH})_2$, for said poly-ε-caprolactone based diol is at least one member selected from the group consisting of straight chain glycols having 2 to 12 carbon atoms; diols having a containing up to 12 carbon atoms and having a side chain, such as neopentyl glycol, 3-methyl-1,5-pentanediol; and diols having an unsaturated group containing up to 12 carbon atoms, such as 3-allyloxy-1,2-propanediol, and wherein said caprolactone unit is present in an average number of 3 to 6.
4. The method for producing a millable polyurethane as claimed in claim 3, wherein said polymerization initiator, $\text{R}_1(\text{OH})_2$, is at least one member selected from the group consisting of straight chain glycols having 2 to 12 carbon atoms, said glycols having no side chain.
5. The method for producing a millable polyurethane as claimed in claim 1 or 2, wherein said polymerization initiator, $\text{R}_1(\text{OH})_2$, is at least one member selected from the group consisting of diols having an aromatic ring, such as 1,4-bis(hydroxyethoxy)benzene and p-xylene glycol; and alicyclic diols, such as cyclohexanediol and cyclohexanedimethanol, and wherein said caprolactone unit is present in an average number of 4 to 8.
6. The method for producing a millable polyurethane as claimed in any one of claims 1 to 5, said polyol further comprises a chain extender.
7. The method for producing a millable polyurethane as claimed in any one of claims 1 to 6, wherein said millable polyurethane has a glass transition temperature, T_g , of no higher than -20°C .
8. The method for producing a millable polyurethane as claimed in any one of claims 1 to 7, wherein said diisocyanate is at least one member selected from the group consisting of 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), and 3,3-dimethyldiphenyl-4,4'-diisocyanate (TODI).
9. The method for producing a millable polyurethane as claimed in any one of claims 1 to 8, wherein said poly-ε-caprolactone based diol is prepared under conditions of no higher than 130°C using a tin catalyst represented by formula (II)



wherein R_2 is a hydrogen atom, an alkyl group, or an aryl group; and X is a hydroxyl group, an alkoxide group or a halogen atom other than fluoride.

10. A method for producing a polyurethane elastomer, comprising the steps:

producing a millable polyurethane according to the method claimed in any one of claims 1 to 9; and
crosslinking said millable polyurethane with a curing agent and molding the resulting cured polyurethane to
form a polyurethane elastomer.

11. The method for producing a polyurethane elastomer as claimed in claim 10, wherein said curing agent is at least one member selected from the group consisting of organic peroxides, sulfur, organic nitrogen-containing compounds, and isocyanate compounds.

12. A polyurethane molded article comprising a mixture of a millable polyurethane prepared by a method as claimed in any one of claims 1 to 9 and a curing agent, said mixture being crosslinked and molded.

13. The polyurethane molded article as claimed in claim 12, wherein said curing agent is at least one member selected from the group consisting of organic peroxides, sulfur, organic nitrogen-containing compounds, and isocyanate compounds.

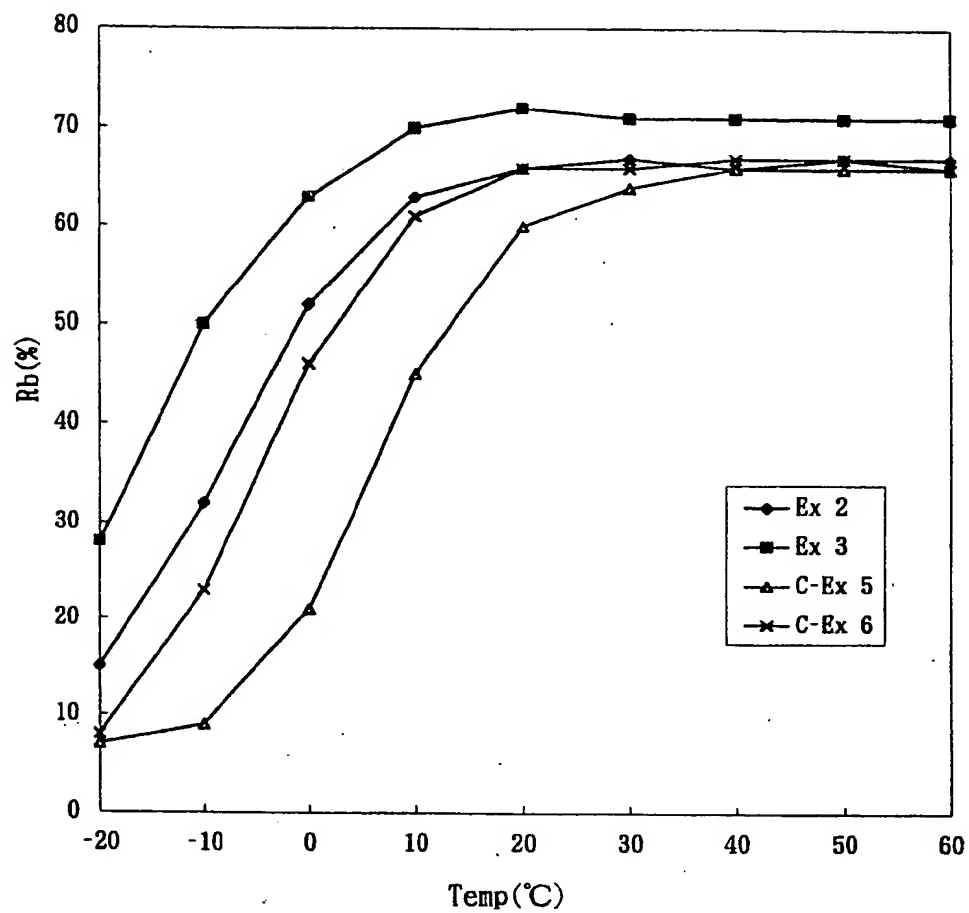


FIG.1

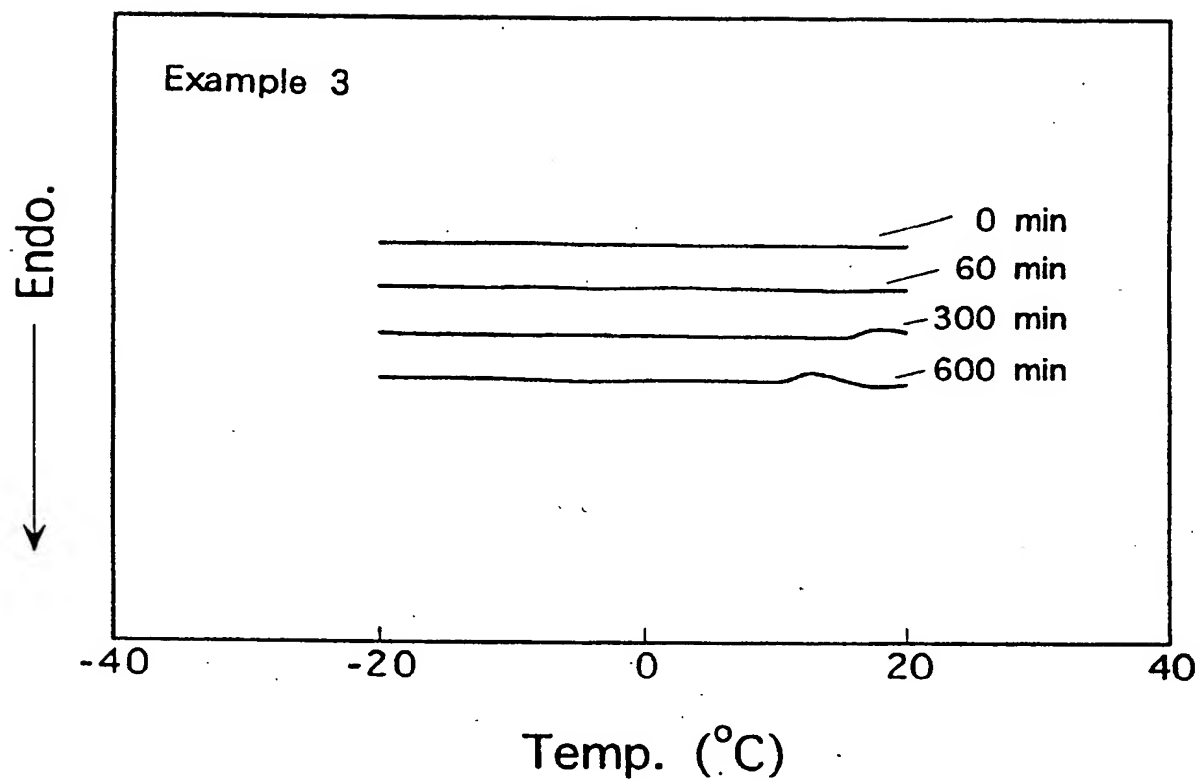


FIG.2

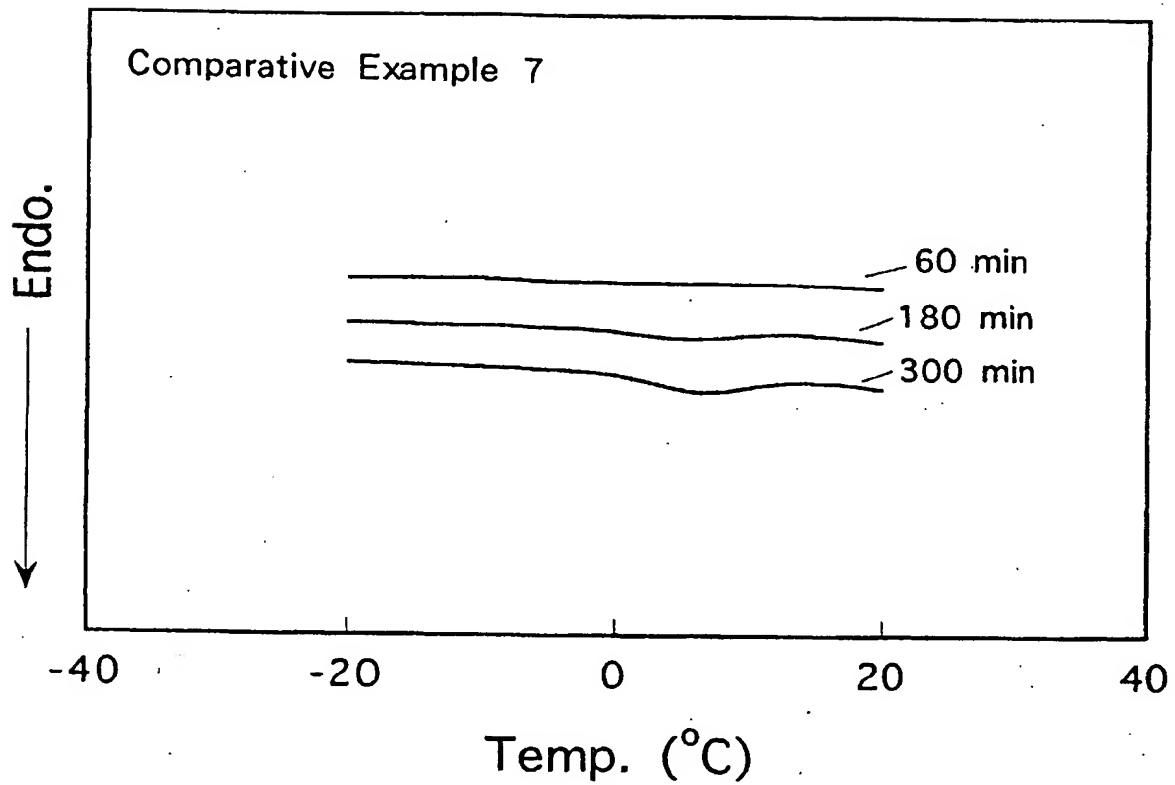


FIG.3

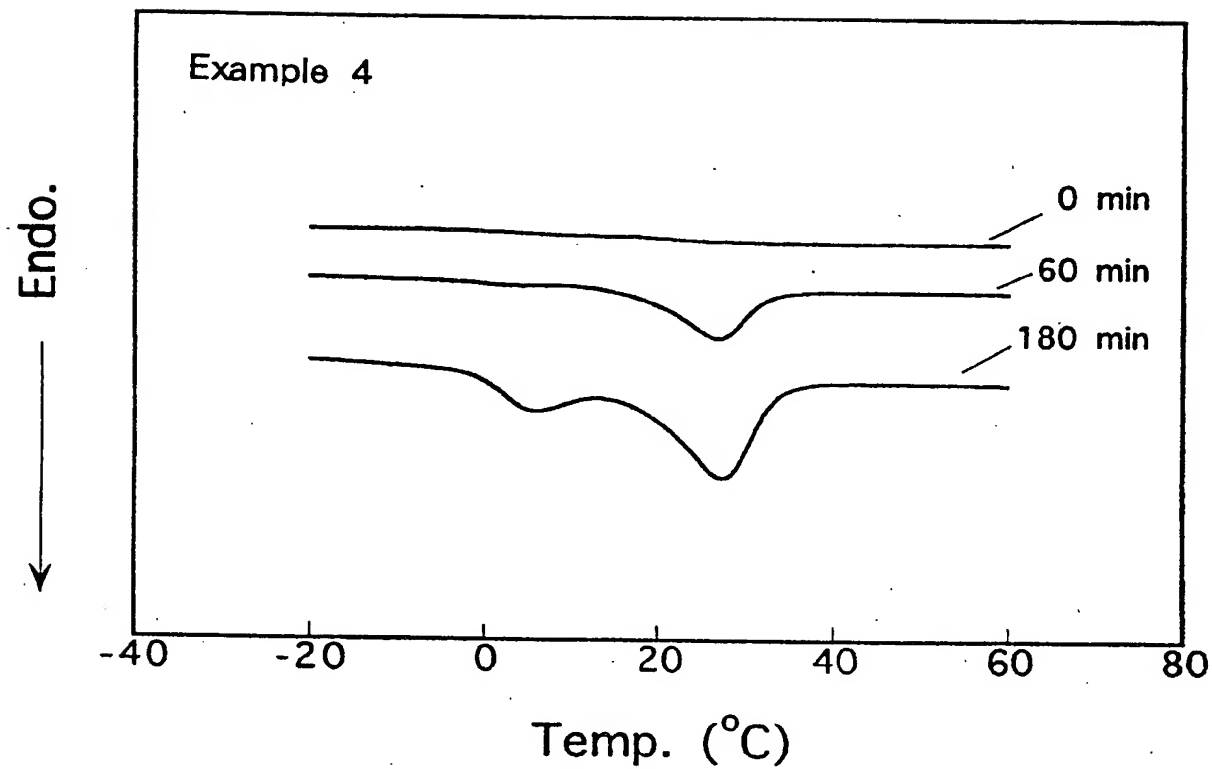


FIG.4

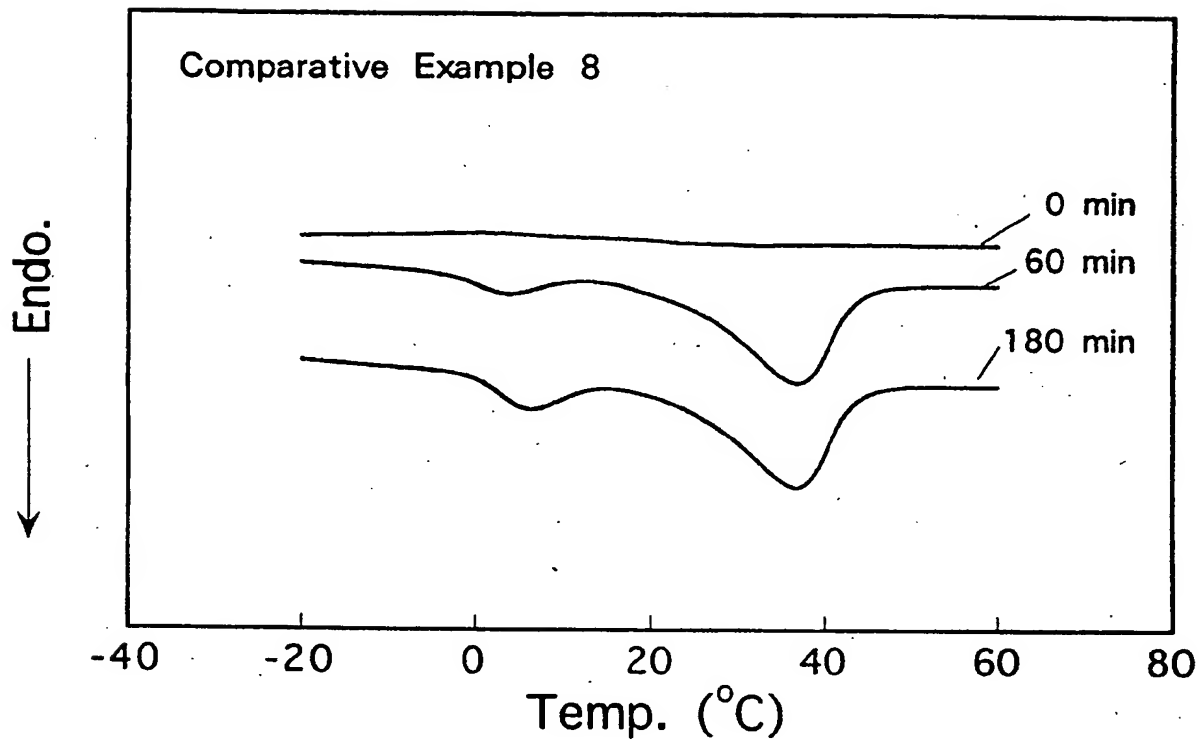


FIG.5

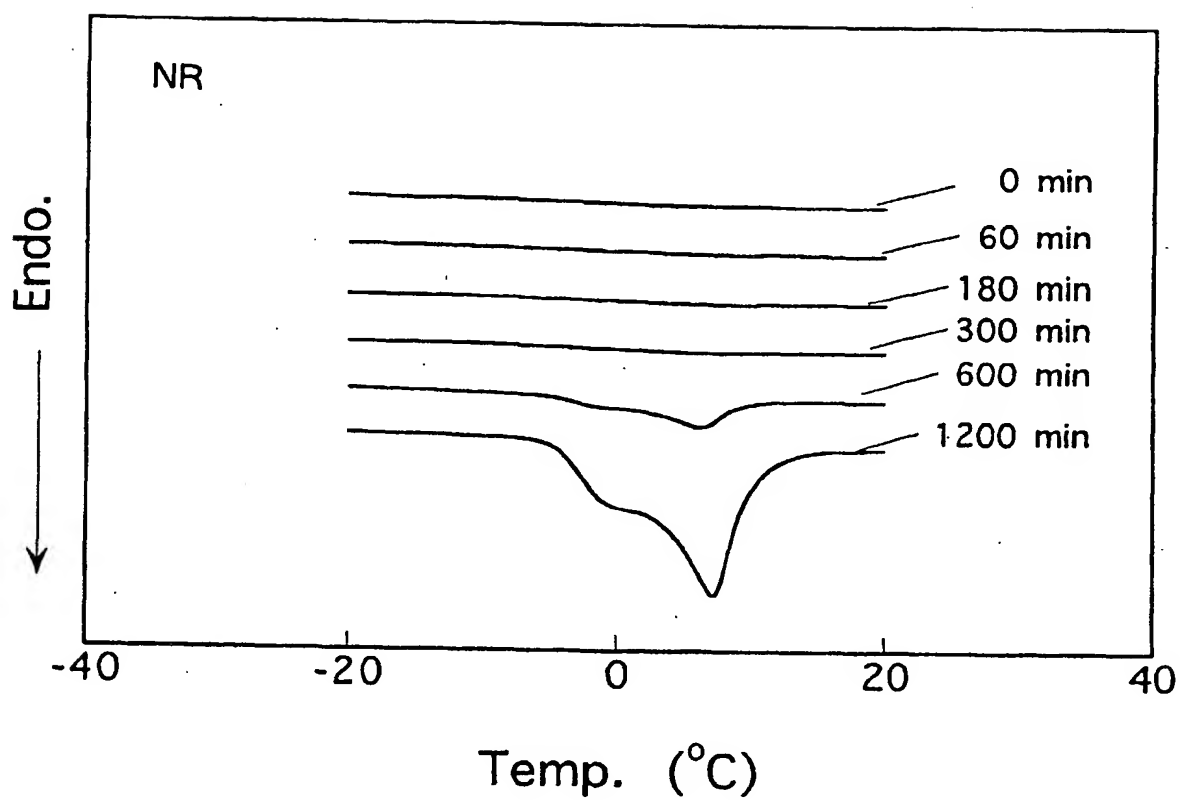


FIG.6

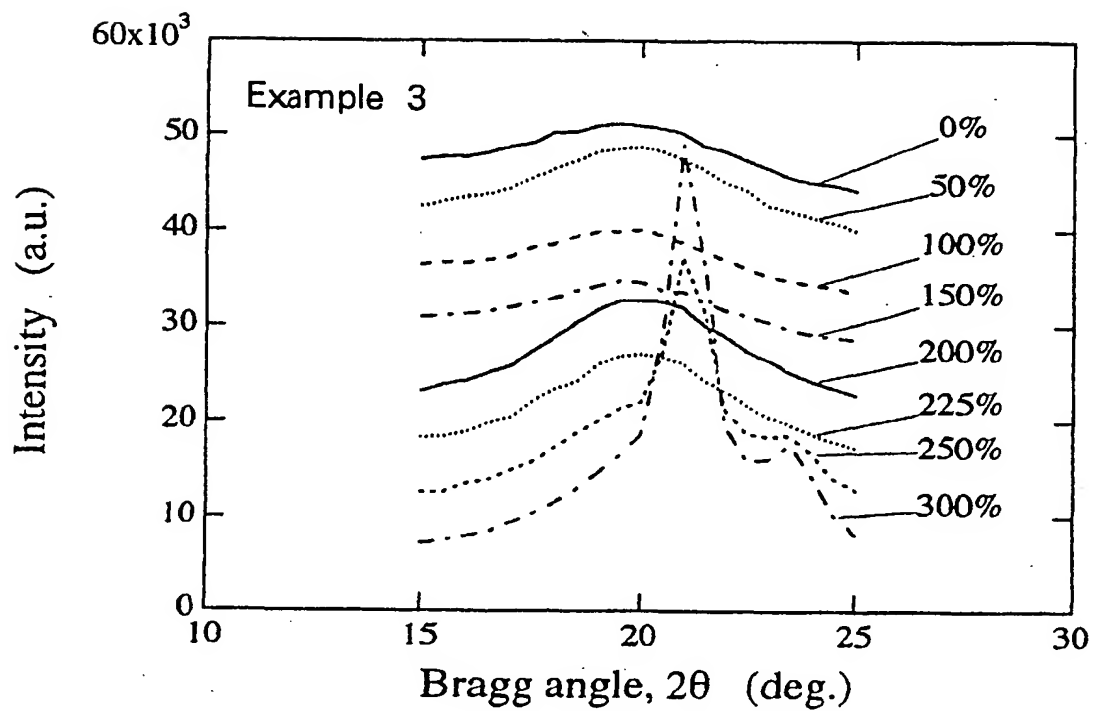


FIG. 7

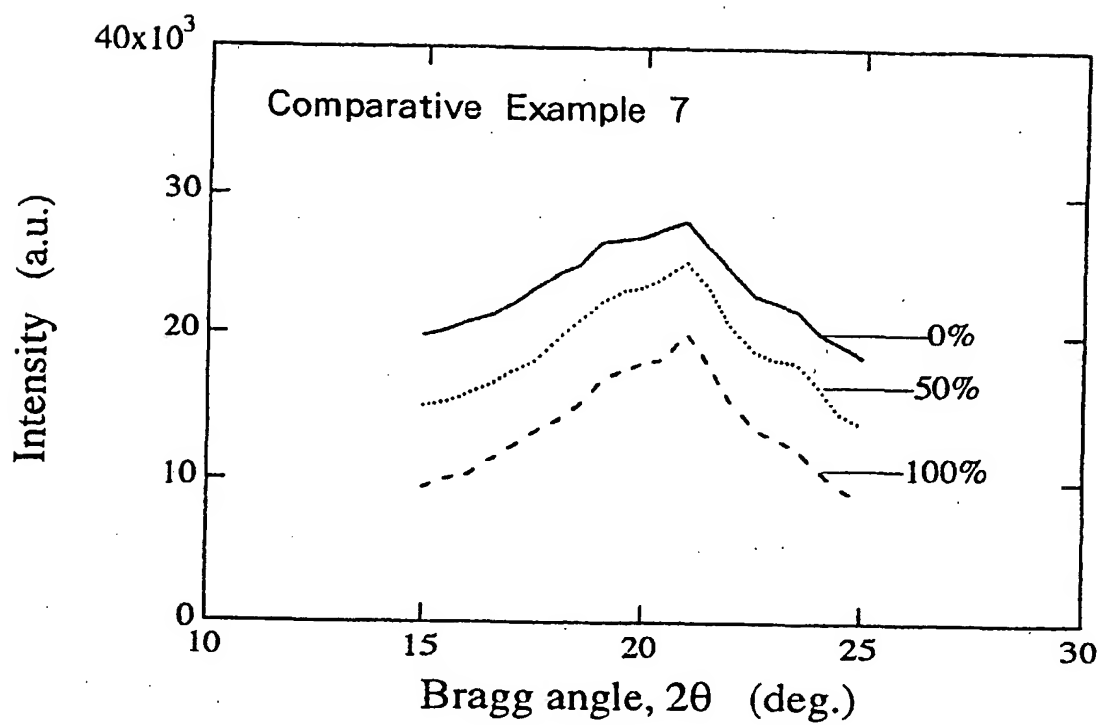


FIG. 8

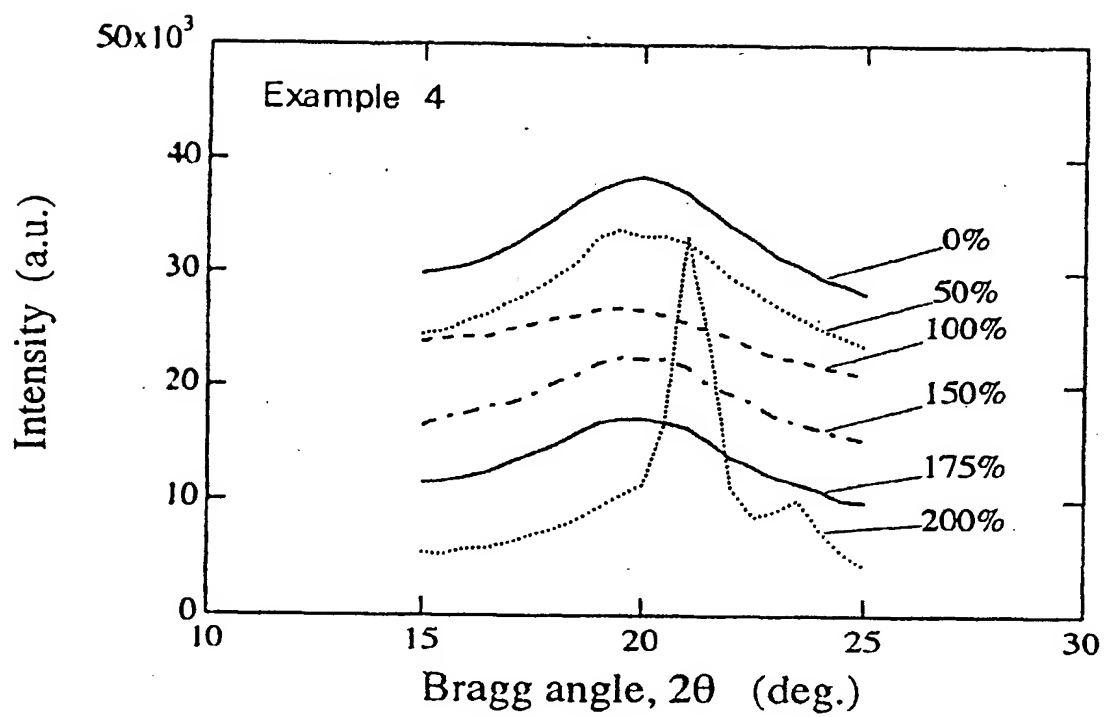


FIG. 9

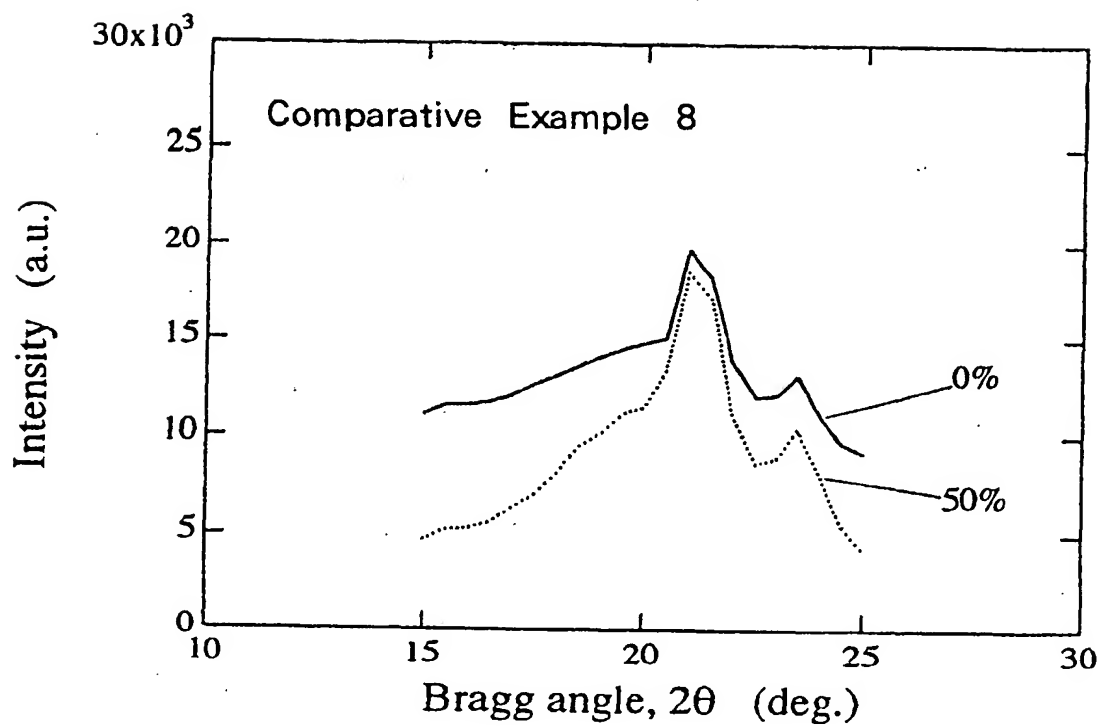


FIG. 10

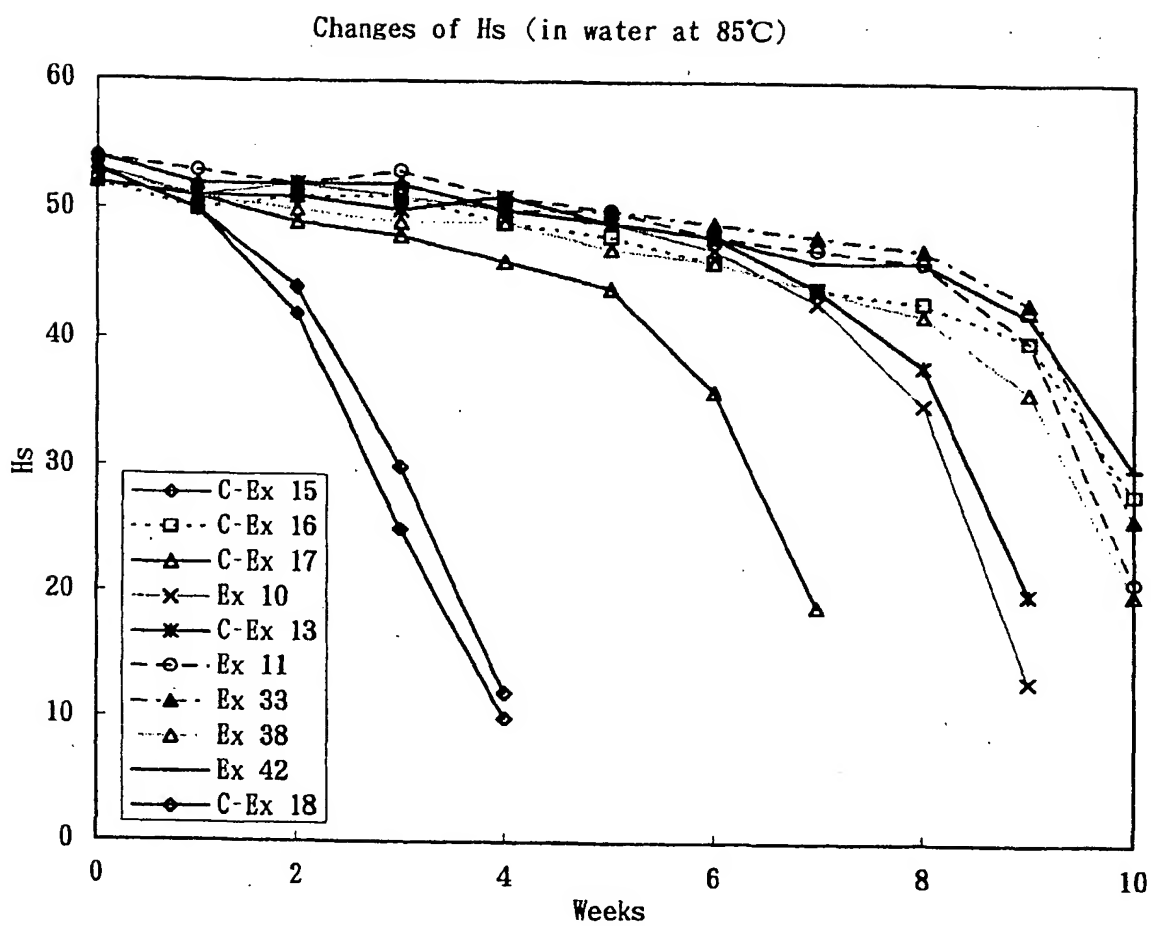


FIG.11

(19)



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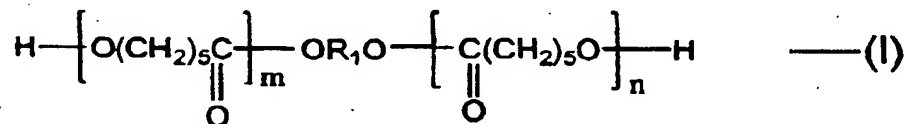
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(54) Method for producing millable polyurethanes and polyurethane elastomers

(57) A method for producing a millable polyurethane, comprises the steps of: producing a poly-ε-caprolactone based diol represented by formula (I)



wherein \square is a caprolactone unit; m and n are numbers of caprolactone units; and R₁ is a divalent group derived from a polymerization initiator of formula R₁(OH)₂, the poly-ε-caprolactone based diol containing a controlled average number of caprolactone units and having a molecular weight distribution Mw/Mn of 1.0 to 1.5; and reacting the poly-ε-caprolactone based diol with a diisocyanate to produce a polyurethane with a restricted crystallizability having a rubber elasticity.

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 May 1997	Examiner Neugebauer, U
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 May 1997	Examiner Neugebauer, U
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